

Examiner's Copy

AN 129:152021 HCA  
TI ~~Tin-silver-copper~~ eutectic alloy modified  
for lead-free solder resistant to fatigue damage  
IN Anderson, Iver E.; Terpstra, Robert L.  
PA Iowa State University Research Foundation, Inc., USA  
SO PCT Int. Appl., 26 pp.  
CODEN: PIXXD2

DT Patent  
LA English

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
	-----	----	-----	-----	-----
PI	WO 9834755	A1	19980813	WO 1998-US2022	19980203
	W: AL, AM, AU, BB, BG, BR, CA, CN, CZ, EE, ES, FI, GE, HU, IS, JP, KG, KP, KR, LK, LR, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, TR, TT, UA, UZ, VN, AM, AZ, BY, KG, KZ, MD, RU, TJ,				
TM					
	RW: GH, GM, KE, LS, MW, SD, SZ, UG, ZW, AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG				
	AU 9860550	A1	19980826	AU 1998-60550	19980203
PRAI	US 1997-796471		19970210		
	WO 1998-US2022		19980203		
AB	The Pb-free solder is <b>Sn-Ag-Cu</b> eutectic alloy contg. <b>Ag</b> 3.5-7.7, <b>Cu</b> 1.0-4.0, and <b>Sn</b> .gtoreq.89%, and is modified with <b>Ni</b> and/or <b>Fe</b> (or similar <b>Cu</b> -compatible metals) at .ltoreq.0.5 each or .ltoreq.1.0% total to increase high-temp. stability of the microstructure and thermomech. fatigue strength without impaired solderability. The modified solder alloys show decreased formation of faceted <b>Cu-Sn</b> intermetallic compds. at the interlayer between the solder and metal substrate, and are suitable for soldering to the <b>Cu</b> conductors on elec. printed-circuit boards. The microstructure of eutectic solder alloy contg. 4.7 <b>Ag</b> and 1.7% <b>Cu</b> with the melting temp. of .apprx.217.degree. was improved by addn. of 0.3% <b>Ni</b> .				

3.5-7.7 Ag

1-4 Cu


≤0.5 Ni

≤0.5 Fe

Sn



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : <b>B23K 35/26</b>		A1	(11) International Publication Number: <b>WO 98/34755</b>
			(43) International Publication Date: 13 August 1998 (13.08.98)
(21) International Application Number: PCT/US98/02022 (22) International Filing Date: 3 February 1998 (03.02.98) (30) Priority Data: 08/796,471          10 February 1997 (10.02.97)          US (71) Applicant: IOWA STATE UNIVERSITY RESEARCH FOUNDATION, INC. [US/US]; 310 Lab of Mechanics, Ames, IA 50011-2131 (US). (72) Inventors: ANDERSON, Iver, E.; 1215 Orchard Drive, Ames, IA 50010 (US). TERPSTRA, Robert, L.; 503 Ely Circle, Ames, IA 50010 (US). (74) Agent: TIMMER, Edward, J.; Walnut Woods Centre, 5955 West Main Street, Kalamazoo, MI 49009 (US).		(81) Designated States: AL, AM, AU, BB, BG, BR, CA, CN, CZ, EE, ES, FI, GE, HU, IS, JP, KG, KP, KR, LK, LR, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, TR, TT, UA, UZ, VN, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  Published With international search report.	
(54) Title: LEAD-FREE SOLDER  <div style="text-align: center;"> <p>Sn-4.7Ag-1.7Cu (Control)</p> <p>DTA T<sub>e</sub> = 216.8 °C          Wetting Angle Mean = 35.25°              Wetting Angle Range = 34-37°</p>  <p>SOLDER — Lu — Cu —</p> <p>Unaged Microstructure</p> </div>			
(57) Abstract  A Sn-Ag-Cu eutectic alloy is modified with one or more low level and low cost alloy additions to enhance high temperature microstructural stability and thermal-mechanical fatigue strength without decreasing solderability. Purposeful fourth or fifth element additions in the collective amount not exceeding about 1 weight % (wt.%) are added to Sn-Ag-Cu eutectic solder alloy based on the ternary eutectic Sn-4.7 % Ag-1.7 % Cu (wt.%) and are selected from the group consisting essentially of Ni, Fe, and like-acting elements as modifiers of the intermetallic interface between the solder and substrate to improve high temperature solder joint microstructural stability and solder joint thermal-mechanical fatigue strength.			

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## LEAD-FREE SOLDER

## CONTRACTURAL ORIGIN OF THE INVENTION

The United States Government has rights in this invention pursuant to Contract No. W-7405-ENG-82 between the U.S. Department of Energy and Iowa State University, Ames, Iowa, which contract grants to Iowa State University Research Foundation, Inc. the right to apply for this patent.

## FIELD OF THE INVENTION

The present invention relates to lead-free solders, solder joints and soldering methods.

## BACKGROUND OF THE INVENTION

The global drive to replace the use of toxic lead metal and its alloys in industrial applications has focused, in part, on the development of new Pb-free solder alloys. In addition to the toxicity of lead, there are other problems concerning continued widespread use of inexpensive Sn-Pb and Pb-based solders. Current leaded solders lack shear strength and resistance to creep and to thermal-mechanical fatigue. A solder which exhibits enhancements of these properties and retains solderability is crucial in automotive and other heavy industry applications where the solder joints are subjected to many thermal cycles, severe vibrations, and sustained temperatures of up to 150 to 170 degrees C. The consequence of solder joint failure in critical applications where "lifetime" performance is now expected can be disastrous.

The excellent metallurgical wetting, or "solderability," of Sn-37%Pb (weight %) is thought to be promoted by the instantaneous formation of a thin layer of a very stable intermetallic compound at the molten solder/base metal interface. Interestingly, the interfacial intermetallic compound that aids solder wetting is always based on Sn (not Pb), e.g., Cu<sub>6</sub>Sn<sub>5</sub> forms at the interface between molten Sn-37%Pb solder and a Cu wire. The role of Pb in promoting solderability is much less understood, but seems related to its ability to strongly suppress the liquid surface tension of the solder alloy, lowering the contact angle of the molten solder which leads to better spreading and more interacting surface area

for the solder joint to form. The eutectic solidification reaction of Sn-37%Pb also generates a highly refined mixture of Sn and Pb phases that produces unusual strength from rather weak constituents, i.e., Sn and, especially, Pb, along with good ductility for forming into wire and foil preforms. Thus, an effective alloy design strategy to develop a Pb-free solder is to start with Sn as the base of the alloy for metallurgical wetting, to add a second or third component to drive wetting and to depress the Sn alloy melting temperature, and to search for a composition that gives a highly-refined, eutectic-like solidification microstructure for an optimum balance of strength and ductility.

One additional design criteria for a Pb-free solder alloy intended for use in severe applications is to significantly improve on the ability of Sn-37%Pb to resist microstructural coarsening, thereby, retain strength and resisting metal fatigue even in high temperature, thermally cycled environments. A Sn-37%Pb solder joint solidification microstructure may start as a finely-spaced eutectic of Sn and Pb solid solution phases but can rapidly coarsen resulting in a lack of shear strength and resistance to creep and to thermal-mechanical fatigue. A new Pb-free solder should utilize microstructural design techniques that inhibit diffusion such as promoting intermetallic second phases formation to strengthen the Sn matrix instead of solid solution hardening or solidification of a finely dispersed primary phase like Bi. Another aspect of microstructural stability that should be addressed is the suppression of growth of the Cu-Sn intermetallic phase layers that initially perform a beneficial function for wetting. Unfortunately, after too much intermetallic growth, the interface between the solder and a Cu substrate can become a weak path for fatigue crack growth. The real need is to develop new Pb-free solders that have similar processing characteristics and usage cost to Sn-Pb and Pb-based solders, but with improved mechanical properties and microstructural stability.

An important industrial consideration is the extensive investment in soldering equipment and manufacturing process design

that is linked to existing leaded solders. This consideration favors the strategy of developing as close to a "drop in" Pb-free solder substitute as possible. In the electrical wiring and electronic packaging industries, a substitute is needed for Sn-37%Pb (wt.%) eutectic solder which melts at 183 degrees C and is commonly used for a broad spectrum of electrically conductive joints. The melting point or liquidus temperature of a new Pb-free solder should be well below the range of adjustment, typically about 280 degrees C maximum, of commercial solder reflow ovens, wave and bath soldering units, and hand soldering guns intended for Sn-Pb solder to allow for a practical amount of superheat, typically 25 to 30 degrees C, during soldering.

One of the primary reasons for the popularity of Sn-37%Pb is its characteristic of excellent wettability and molten fluidity, or "solderability" when forming a solder joint on common metals, like Cu, steel, brass, and stainless steel. A eutectic solder alloy like Sn-37%Pb exhibits maximum fluidity as soon as melting begins because it has no "mushy" melting range. Effective soldering with Sn-37%Pb usually requires only a mild flux to remove surface oxides and to start the metallurgical solder wetting and bond formation in an ambient air environment. A large effort in the electronics industry to eliminate the use of CFC-based cleaning agents has led to the universal push to ever milder fluxes that do not require post-reflow cleaning. Thus, any new Pb-free solder must be compatible with very mild fluxes. Also, any new Pb-free solder should not be sensitive to air oxidation.

The soldering needs of the heat exchanger industry, supplying automotive and industrial vehicle radiators, as well as industrial and residential climate control systems, and many other heavy industrial applications, such as hydraulic and pneumatic hose fittings connections, are perhaps broader and consume larger quantities of elemental Pb. This higher Pb consumption is because of the much broader use of Pb-based solders compared to Sn-37%Pb solder, especially, Pb-5%Sn solder, which melts gradually between 305 degrees C and 316 degrees C. The Pb-5%Sn solder is commonly

used for initial bath dip soldering of copper radiator cores and for some header and tank seams involving brass and steel. Sn-37%Pb is used only for secondary seams and finishing. The important solder properties in these applications are general mechanical durability, chemical stability, and thermal conductivity. The poor corrosion resistance and fatigue strength of Pb-5%Sn solder, particularly during pressurization cycles at temperatures of about 120 degrees C, are the primary property deficiencies that must be overcome by a Pb-free solder replacement. Solder alloy ingot and wire cost is a much more important criteria for heat exchanger manufacturing than for electronics, and any replacement for ultra-low cost Pb-5%Sn solder must be applied more efficiently, probably as a paste or preform foil, to compete on total manufacturing cost, even if significantly improved properties can be demonstrated.

A Pb-free ternary eutectic solder alloy, Sn-4.7%Ag-1.7%Cu (weight %) is described in U.S. Patent No. 5,527,628, issued June 18, 1996, which exhibits a melting point of 217 degrees C and very good solderability. This solder alloy liquid solidifies as a fine eutectic microstructure of Cu<sub>3</sub>Sn, and Ag<sub>3</sub>Sn intermetallic phases dispersed in a Sn(bct) matrix when cooled under typical solder reflow conditions, a microstructure which is significantly stronger than that of Sn-Pb eutectic solder. A Sn-Ag-Cu ternary eutectic had not been reported in previous experimental or calculated phase diagram studies and initial test results show great promise for this alloy as a Pb-free solder. The only significant deficiency of the Sn-Ag-Cu eutectic solder appeared to be a susceptibility to intermetallic layer growth at the solder/Cu substrate interface, particularly at high aging temperatures, a feature that is shared by essentially all high-Sn, Pb-free solders.

#### SUMMARY OF THE INVENTION

The present invention relates to a modification of the aforementioned Sn-Ag-Cu ternary eutectic Pb-free solder alloy and variants thereof with one or more low level and low cost alloy additions to enhance high temperature microstructural stability and thermal-mechanical fatigue strength without decreasing

solderability. In one embodiment, fourth or fifth element additions in the collective amount of about 1 weight % or less are made to Sn-Ag-Cu solder alloys based on the ternary eutectic Sn-4.7% Ag-1.7% Cu (weight %) as well as variants thereof and are selected from the group consisting essentially of Ni, Fe, and like-acting elements. The additive element(s) act as a beneficial modifier(s) of the solder/substrate interface. Particularly, the addition of one or more additive elements beneficially modifies the morphology and suppresses growth rate of an intermetallic interface layer under high temperature aging conditions to enhance high temperature microstructural stability and thermal-mechanical fatigue strength without decreasing solderability.

The present invention also envisions the possible reduction of the Ag content of the base ternary eutectic alloy, Sn-4.7% Ag-1.7% Cu (wt.%) and variants thereof, to lower the alloy cost without significant penalties in microstructural stability, increased pasty range (retaining a pasty range of less than 15 degrees C), high temperature performance, and solderability. A modified range for silver content of these alloys extends from about 4.7 wt.% to about 3.0 wt. %. To produce a suitable solder microstructure, the Cu content can be lowered along with the Ag content to a minimum of about 0.5 wt % to account for the additive additions without promoting formation of large intermetallic phases in the body of the as-solidified solder. In other words the solder microstructure will retain the fine, uniform microstructure commonly associated with eutectic alloys. To accomplish this the ratio of Ag to Cu+X (where X = Ni, Fe, and like-acting elements) should remain similar to the Ag/Cu ratio in the Sn-Ag-Cu eutectic.

#### DESCRIPTION OF THE DRAWINGS

Figure 1a is a photomicrograph at 500X of an unaged solder joint sample made using a control ternary eutectic Sn-4.7% Ag-1.7% Cu solder alloy, while Figure 1b is a similar photomicrograph of the solder joint aged as described below.

Figure 2a is a photomicrograph at 500X of an unaged solder joint sample made using a 0.15 weight % Ni modified eutectic solder alloy



pursuant to the invention, while Figure 2b is a similar photomicrograph of the solder joint aged as described below.

Figure 3a is a photomicrograph at 500X of an unaged solder joint sample made using a 0.3 weight % Fe modified eutectic solder alloy pursuant to the invention, while Figure 3b is a similar photomicrograph of the solder joint aged as described below.

Figure 4a is a photomicrograph at 500X of an unaged solder joint sample made using a 0.3 weight % Ni modified eutectic solder alloy pursuant to the invention, while Figure 4b is a similar photomicrograph of the solder joint aged as described below.

Figure 5a is a photomicrograph at 500X of an unaged solder joint sample made using a 0.3 weight % Ni modified eutectic solder alloy having an off-eutectic base composition pursuant to the invention, while Figure 5b is a similar photomicrograph of the solder joint aged as described below.

#### DETAILED DESCRIPTION OF THE INVENTION

The aforementioned modified solder alloys of the present invention establish a new family of robust Pb-free solders that can operate or be exposed at temperatures up to about 170 degrees C for example in service and which can substitute widely for Sn-Pb eutectic and Pb-based solders in manufacturing and repair operations. The solder is free of lead and the products of lead mining and refining. The solder components are of low cost, with the exception of Ag, and are all widely available with ample ore reserves.

The modified Sn-Ag-Cu ternary eutectic alloy and variants thereof pursuant to the present invention include one or more low level and low cost alloy additions to enhance high temperature microstructural stability and thermal-mechanical fatigue strength without decreasing solderability. In particular, purposeful or intentional fourth, fifth or more element additions in a collective amount of about 1 weight % (wt.%) or less of the solder alloy composition are made to the ternary eutectic Sn-Ag-Cu solder alloy based on the ternary eutectic Sn-4.7% Ag-1.7% Cu (weight %) as well as variants thereof. The additive elements are selected from the

group consisting of Ni, Fe, and like-acting elements that beneficially modify the morphology and/or suppress growth of the intermetallic interface, especially from high temperature aging, in a manner to improve high temperature microstructural stability and thermal-mechanical fatigue strength without decreasing solderability. In addition to nickel and iron, other like-acting additive elements to this end include cobalt which is less preferred as a result of its relatively high cost and uncertain availability. Each additive element may be present alone in an amount of at least about 0.01 weight % and preferably not exceeding about 0.5 weight % of the solder alloy composition. The addition of one or more of the additive elements modifies the morphology of the as-solidified intermetallic interface typically containing a thin layer of  $\text{Cu}_6\text{Sn}_5$ , with the soldered substrate or component typically being Cu, in particular to reduce the thickness of the as-solidified intermetallic interface. More importantly, the addition of one or more of the additive elements modifies the morphology and suppresses the growth rate of high temperature aged intermetallic interface, typically containing Cu based layers of  $\text{Cu}_6\text{Sn}_5$  and  $\text{Cu}_3\text{Sn}$ , with the substrate or component typically being Cu. The morphology modification appears to be accomplished by a mechanism which acts to destroy the preferential growth facets or surfaces of the intermetallic interface to instead permit more unfaceted, non-planar interface growth surfaces, although Applicants do not wish or intend to be bound by any theory in this regard. The growth suppression appears to be accomplished by a mechanism which acts to limit diffusive transport of Cu from the substrate or component to the growing intermetallic layers because of additional strains imposed on the intermetallic phases by the substitutional additions, although Applicants do not wish or intend to be bound by any theory in this regard. Also, the limited diffusive transport of Cu from the substrate or component into the body of the solder achieved through the addition of one or more additive elements serves to limit the formation and excessive growth of near-interface intermetallic phases, primarily  $\text{Cu}_6\text{Sn}_5$ , in

the solder microstructure.

The modified solder alloy of the present invention exhibits a melting temperature of about 217 degrees C with a liquid-solid temperature "pasty" range relative to the melting temperature not exceeding 15 degree C, preferably not exceeding about 5 degrees C above the melting temperature. For electronic solder applications using solder reflow procedures, the melting temperature range (liquid plus solid phases) of the solder of the invention is extended no more than 15 degrees C above the ternary eutectic melting temperature. In particular, such solder reflow procedures involve general heating of a wiring board to temperatures of about 230 to 250 degrees C. Solders used in the such solder reflow procedure desirably exhibit a limited melting range (i.e. liquid-solid "mushy" zone) less than about 15 degrees C.

A particular modified Sn-Ag-Cu-X solder alloy of the present invention consists essentially of, in weight %, about 3.5 to about 7.7 weight % Ag, about 1.0 to about 4.0 weight % Cu, intentional addition of one or more of Ni, Fe and like-acting additive elements in a collective amount of about 1 weight % (wt.%) or less, and balance essentially Sn. A particular modified Sn-Ag-Cu-X solder alloy of the present invention lean in silver consists essentially of, in weight %, about 4.0 to about 3.0 weight % Ag, about 4.0 weight to about 0.5 weight % Cu, intentional addition of one or more of Ni, Fe and like-acting additive elements in a collective amount of about 1 weight % (wt.%) or less, and balance Sn where Sn is preferably present in an amount of at least about 89 weight % Sn of the solder alloy. The ratio of Ag to Cu + X (where X = Ni, Fe, and like-acting elements) in the modified solder alloys of the present invention should remain similar to the Ag/Cu ratio in the Sn-Ag-Cu eutectic; i.e., about  $\text{Ag/Cu} + \text{X} = 3/1$ .

$\leq 1\% \sum (\text{Ni, Fe})$

The modified Sn-Ag-Cu-X solder alloy of the present invention can be made in the manner described in U.S. Patent 5 527 628, the teachings of which are incorporated herein by reference. The solder alloy can be made and used in various forms such as solder wire, sheet, foil, ingot, powder and others. Solder powder of the

invention can be incorporated into electronic solder paste for use in circuit assembly by means of surface mount technology. Solder flux formulations for all forms of the solder of the invention can be selected from commercially available flux products or as developed for particular applications.

The melting behavior of the modified solder alloys of the present invention is that of a near-eutectic alloy with a pasty range (liquid plus solid temperature range) typically less than 5 degrees C and certainly less than 15 degrees C. The start of solder alloy melting will occur at about 217 degrees C, which is the eutectic melting temperature of the base Sn-4% Ag-1.7% Cu (weight %) eutectic alloy. These melting temperatures can be tolerated by many existing components and circuit boards and should be compatible with conventional reflow ovens, soldering irons, and other solder melting devices.

The as-solidified solder microstructure is essentially a fine eutectic mixture of intermetallic phases,  $\text{Cu}_6\text{Sn}_5$  and  $\text{Ag}_3\text{Sn}$ , dispersed in a Sn matrix upon solidification at conventional cooling rates (1 to 10 degrees C/second) for soldering operations. The additions of additive element(s) described above may dissolve into the Cu-based intermetallic phases present in the solder microstructure according to analysis of the metallic radii of the additives; i.e. Ni and Fe, where the radii do not differ by more than about 3% from the Cu atom (see Table I.), although Applicants do not wish or intend to be bound by any theory in this regard. This is well within the alloy design criteria of about 10% deviation for expected significant (5 atomic %) solid solubility reported by Hume-Rothery.

Table I.

Element	Metallic Radius (angstroms)	Radius Mismatch
Cu	1.278	0 (base)
Fe	1.274	-0.3%
Ni	1.246	-2.6%

The additive elements within the solder body and at the substrate (e.g., Cu)/solder interface serve to beneficially modify the morphology and suppress the growth rate of the Cu based intermetallics during high temperature aging. The morphology modification is especially important at the solder/Cu solder interface where the interface morphology of the invention after aging adopts a more unfaceted non-planar more even growth surface. Such an interface will resist both tensile and shear stresses far better than the regularly faceted interfaces common for most Sn-based solders. Thus, when loaded in either constant stress, i.e., creep conditions, or in cyclic stress, i.e., fatigue conditions, the solder microstructure of this invention will display significantly improved creep and fatigue resistance.

The elevated temperature aged intermetallic interface of the solders of the invention will advance at a reduced rate which minimizes interface layer thickness and reduces the extent of the solute depleted zone adjacent to the interface in the body of the solder microstructure. A solute depleted zone will consist essentially of pure Sn which has a significantly reduced strength. Both of these features, a thinner intermetallic interface for a given aging exposure and a reduced solute depleted zone, will also improve the resistance of such solder joints to creep and fatigue failures.

The minimization of Cu diffusion through the intermetallic interface that appears to be promoted by the solder alloy of this invention also results in a significant reduction of near-interface large intermetallic precipitate phases in the solder microstructure. The presence of these large, sharp-edged intermetallic particles, typically  $\text{Cu}_3\text{Sn}$ , in most Sn-based solders after aging can encourage fatigue crack nucleation. The significant reduction or in some cases lack of such precipitates will further promote extended fatigue resistance in the solder alloys of this invention.

No viable alternatives to this invention are known to perform at the same temperatures with equivalent properties and be composed of

similarly suitable components with such ease of processing.

The following Examples are offered to better illustrate the present invention without in any way limiting the scope thereof.

#### EXAMPLES:

Alloys (in wt. %) of the following compositions:

99.7%(Sn-4.7% Ag-1.7% Cu) + 0.3% Ni

99.85%(Sn-4.7% Ag-1.7% Cu) + 0.15% Ni

99.7%(Sn-4.7% Ag-1.7% Cu) + 0.3% Fe

99.7%(Sn-3.6% Ag-1.0% Cu) + 0.3% Ni

were made and subjected to the following tests:

Differential thermal analysis (DTA) was conducted to determine melting behavior (solidus temperature and liquidus temperature) of the solder.

Solder joint samples (drops) were melted and solidified on Cu substrate (i.e. soldered component) using RMA (rosin mildly active) flux (Alpha 611 flux from Alpha Metals, Jersey City, New Jersey) and quenched in silicone vacuum pump oil (Dow 200) to get a uniform as-solidified microstructure because of the constant cooling rate of 5 to 10 degrees C/second which is typical of industrial soldering operations (paste reflow and hand soldering with a soldering iron).

As-solidified microstructure of each sample was examined to verify resemblance to the eutectic microstructure and substrate/solder interface morphology described above.

Solder joint samples annealed (aged) in air atmosphere furnace at 170 degrees C for about 2 days to simulate severe temperature exposure, for example, experienced by exposure of the solder joint in service to 170 degrees C for extended times. A control sample of the aforementioned unmodified Sn-Ag-Cu eutectic alloy of U.S.

Patent 5 527 628 was included for direct comparison.

Aged microstructure of each sample was examined to verify modification of interface aging characteristics and near-interface solder microstructure features.

Figure 1a is a photomicrograph of an unaged solder joint sample made using the aforementioned control ternary eutectic Sn-4.7% Ag-1.7% Cu solder alloy (weight %), while Figure 1b is a similar photomicrograph of the solder joint of Figure 1a aged as described above. This solder sample provides a comparison for the solder joint samples made pursuant to the present invention and discussed below.

Figure 2a is a photomicrograph of an unaged solder joint sample made using a 0.15 weight % Ni modified eutectic solder alloy pursuant to the invention, while Figure 2b is a similar photomicrograph of the solder joint sample aged as described above.

Figures 3a (unaged solder joint) and 3b (aged solder joint) are similar photomicrographs for a 0.3 weight % Fe modified eutectic solder alloy joint pursuant to the invention.

Figure 4a (unaged solder joint) and 4b (aged solder joint) are similar photomicrographs for a 0.3 weight % Ni modified eutectic solder alloy joint sample pursuant to the invention.

Figure 5a (unaged solder joint) and 5b (aged solder joint) are similar photomicrographs for a 0.3 weight % Ni modified eutectic solder alloy joint sample having an off-eutectic (Sn-3.6% Ag-1.0% Cu) base composition pursuant to the invention.

The joint samples of Figures 2-5 had solder compositions that corresponded to those set forth above under EXAMPLES.

In Figures 1-5, the thickest as-solidified (unaged) Cu based intermetallic interface layer  $L_u$  was observed in the microstructures of the control solder joint sample. Similarly, the thickest aged intermetallic interface layer  $L_a$  was observed in the microstructures of the aged control solder joint sample. In Figures 1-5, unaged interface layer  $L_u$  was likely  $Cu_6Sn_5$ , while aged interface layers  $L_a$  were likely  $Cu_6Sn_5$  (light gray phase layer with layer regions extending into the solder body in Figures 1b-5b) and

Cu<sub>3</sub>Sn (darker gray phase layer adjacent Cu substrate in Figures 1b-5b). In Figures 1-5, the black line(s) or line segments adjacent the intermetallic interface layer L is/are polishing and etching artifacts.

In all solder joint samples examined, the unaged joint microstructures exhibited a thinner intermetallic interface layer L<sub>u</sub> as compared to the aged interface layers L<sub>a</sub> present in the aged solder joint microstructures.

Comparing Figures 2b-5b to Figure 1b, it is apparent that the aged intermetallic interface layers (Cu<sub>3</sub>Sn<sub>1</sub> and Cu<sub>3</sub>Sn<sub>2</sub>) of the solder joint samples made pursuant to the invention exhibited significantly reduced faceted, planar angular growth surfaces or regions extending into the solder body, which reduction will enhance high temperature solder joint microstructural stability and thermal-mechanical fatigue solder joint strength. In the solder joint samples of the invention of Figures 2b-5b, the interface layer adopted a more unfaceted, more even growth interface surface or morphology. Moreover, these beneficial interface features were achieved without substantially decreasing solderability as evaluated by measured DTA liquidus and solidus temperatures ( $T_L$  and  $T_S$ , both in degrees C) and wetting angle mean and range (degrees). For example, in Figures 2-5, the DTA liquidus and solidus temperatures measured as well as the wetting angle mean and wetting angle range are set forth for comparison to similar data measured for the control sample joint. For the control sample of Figure 1, the  $T_L$  was approximately 216.8 degrees C and the wetting angle mean was approximately 35.25 degrees and wetting angle range was approximately 34-37 degrees. For the 0.15% Ni modified solder alloy of Figure 2, the  $T_L$  and  $T_S$  were approximately similar to those of the control ternary eutectic sample and the wetting angle mean was approximately 30.0 degrees and wetting angle range was approximately 28-34 degrees. For the 0.3% Fe modified solder alloy of Figure 3, the  $T_L$  and  $T_S$  were approximately similar to those of the control ternary eutectic sample and the wetting angle mean was approximately 36.5 degrees and wetting angle range was



approximately 27-45 degrees. For the 0.3% Ni modified solder alloy of Figure 4, the  $T_c$  and  $T_i$  were approximately similar to those of the control ternary eutectic sample and the wetting angle mean was approximately 23.75 degrees and wetting angle range was approximately 17-27 degrees. For the 0.3% Ni modified solder alloy of Figure 5, the  $T_c$  and  $T_i$  were approximately similar to those of the control ternary eutectic sample and the wetting angle mean was approximately 30.0 degrees and wetting angle range was approximately 29-32 degrees.

While the present invention has been described in terms of specific embodiments thereof, it is not intended to be limited thereto but rather only to the extent set forth hereafter in the following claims.

## CLAIMS:

## We Claim:

1. In a Pb-free solder consisting essentially of a eutectic composition consisting essentially of, in weight %, about 93.6 weight % Sn-about 4.7 weight % Ag-about 1.7 weight % Cu having a eutectic melting temperature of about 217 degrees C and variants thereof wherein the concentrations of Sn, Ag, and Cu deviate from said eutectic composition to provide a controlled melting temperature range not exceeding about 15 degrees C above said eutectic melting temperature, the improvement comprising an additive element selected from the group consisting essentially of Ni, Fe and like-acting elements present in said solder alloy in an amount effective to modify an intermetallic interface between the solder and a substrate to improve solder joint strength.
2. The solder of claim 1 wherein the additive element is present in an amount effective to reduce amount of a faceted Cu-Sn intermetallic interface between the solder and the substrate.
3. The solder of claim 1 which consists essentially of, in weight %, about 3.5 to about 7.7 weight % Ag, about 1.0 to about 4.0 weight % Cu, intentional addition of one or more of Ni, Fe and like-acting elements in an individual amount not exceeding about 0.5 weight % or collective amount not exceeding about 1.0 weight %, and balance essentially of Sn.
4. The solder alloy of claim 3 where Sn is present in an amount of at least about 89 weight % Sn of the alloy.
5. The solder alloy of claim 1 wherein the ratio of Ag/Cu + X where X = Ni, Fe, and like-acting additive element is about 3 to 1.

6. The solder of claim 1 which consists essentially of, in weight %, about 4.0 to about 3.0 weight % Ag, about 4.0 weight to about 0.5 weight % Cu, intentional addition of one or more of Ni, Fe and like-acting elements in an individual amount not exceeding 0.5 weight % or a collective amount not exceeding about 1 weight %, and balance essentially of Sn.

7. The solder alloy of claim 6 where Sn is present in an amount of at least about 89 weight % Sn of the alloy.

8. The solder alloy of claim 6 wherein the ratio of Ag/Cu + X where X = Ni, Fe, and like-acting additive element is about 3 to 1.

9. In a solder joint comprising a eutectic composition consisting essentially of, in weight %, about 93.6 weight % Sn-about 4.7 weight % Ag-about 1.7 weight % Cu having a eutectic melting temperature of about 217 degrees C and variants thereof wherein the concentrations of Sn, Ag, and Cu deviate from said ternary eutectic composition to provide a controlled melting temperature range not exceeding about 15 degrees C above said eutectic melting temperature, the improvement comprising an additive element selected from the group consisting essentially of Ni, Fe and like-acting elements present in said solder alloy in an effective amount to modify an intermetallic interface between the solder and a soldered component to improve solder joint strength.

10. The solder joint of claim 9 wherein the additive element is present in an amount effective to reduce amount of a faceted Cu-Sn intermetallic interface between the solder and the component.

11. In a soldering process for a component by solidifying a molten solder Pb-free solder consisting essentially of, in weight %, about 93.6 weight % Sn-about 4.7 weight % Ag-about 1.7 weight % Cu having a eutectic melting temperature of about 217 degrees C and variants thereof wherein the concentrations of Sn, Ag, and Cu deviate from said ternary eutectic composition to provide a controlled melting temperature range not exceeding about 15 degrees C above said eutectic melting temperature, the improvement comprising including in said solder alloy an additive element selected from Ni, Fe and like-acting elements in an effective amount to modify an intermetallic interface between the solder and the component to improve solder joint strength.

12. The process of claim 11 which consists essentially of, in weight %, about 3.5 to about 7.7 weight % Ag, about 1.0 to about 4.0 weight % Cu, intentional addition of one or more of Ni, Fe and like-acting elements in an individual amount not exceeding about 0.5 weight % or a collective amount not exceeding about 1 weight %, and balance essentially of Sn.

13. The process of claim 12 where Sn is present in an amount of at least about 89 weight % Sn of the alloy.

14. The process of claim 12 wherein the ratio of Ag/Cu + X where X = Ni, Fe, and like-acting additive element is about 3 to 1.

15. The process of claim 11 which consists essentially of, in weight %, about 4.0 to about 3.0 weight % Ag, about 4.0 weight to about 0.5 weight % Cu, intentional addition of one or more of Ni, Fe and like-acting elements in an individual amount not exceeding about 0.5 weight % or a collective amount not exceeding about 1 weight %, and balance essentially of Sn.

16. The process of claim 15 where Sn is present in an amount of at least about 89 weight % Sn of the alloy.

17. The process of claim 15 wherein the ratio of Ag/Cu + X where X = Ni, Fe, and like-acting additive element is about 3 to 1.
18. The process of claim 11 wherein the additive element is present in an amount effective to reduce amount of a faceted Cu-Sn intermetallic interface between the solder and the component.
19. The process of claim 11 wherein the molten solder is solidified in contact with a copper electrical component.

1/5

Sn-4.7Ag-1.7Cu  
(Control)

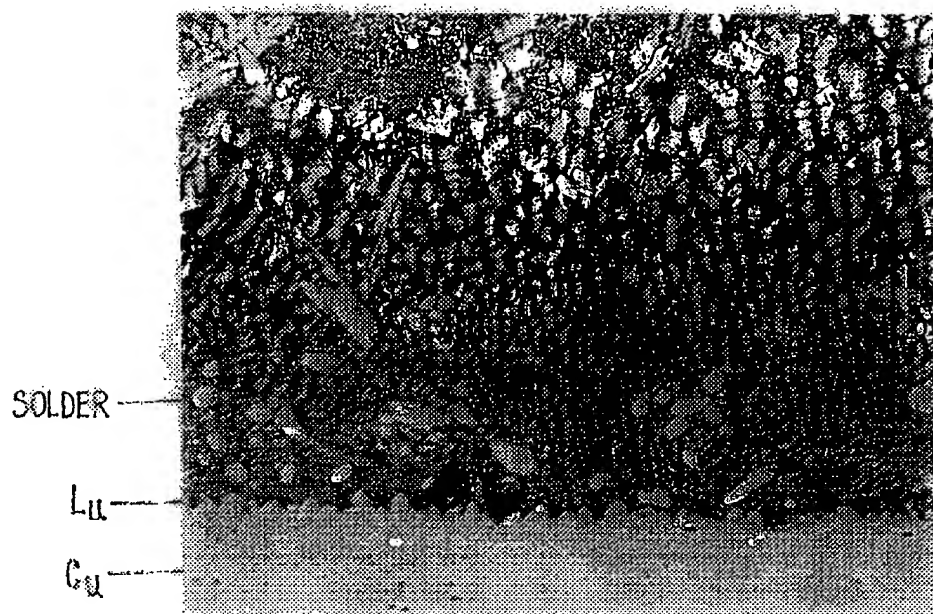
DTA  $T_s = 216.8^\circ\text{C}$ Wetting Angle Mean =  $35.25^\circ$ Wetting Angle Range =  $34-37^\circ$ 

FIG. 1A

Unaged Microstructure

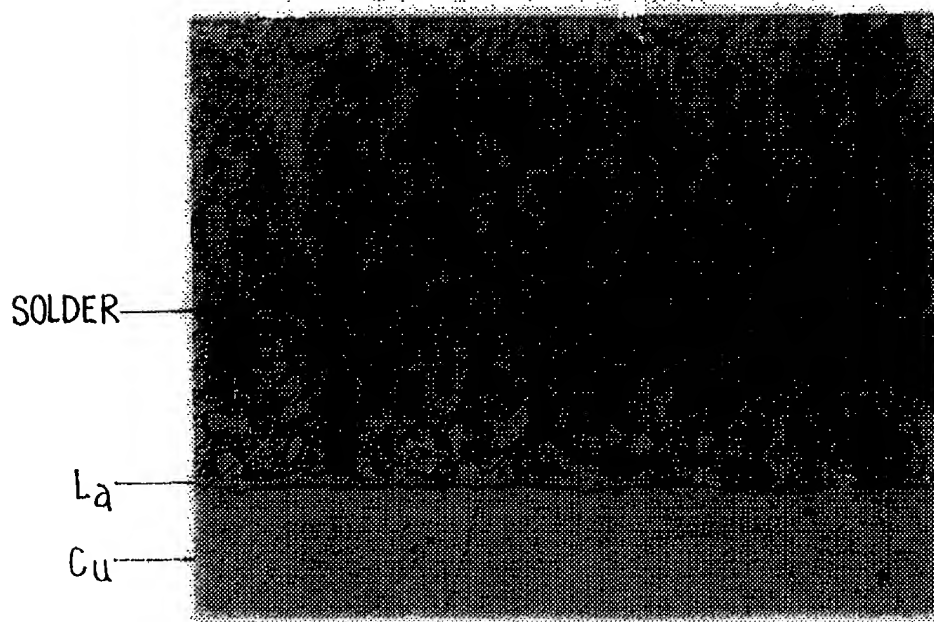
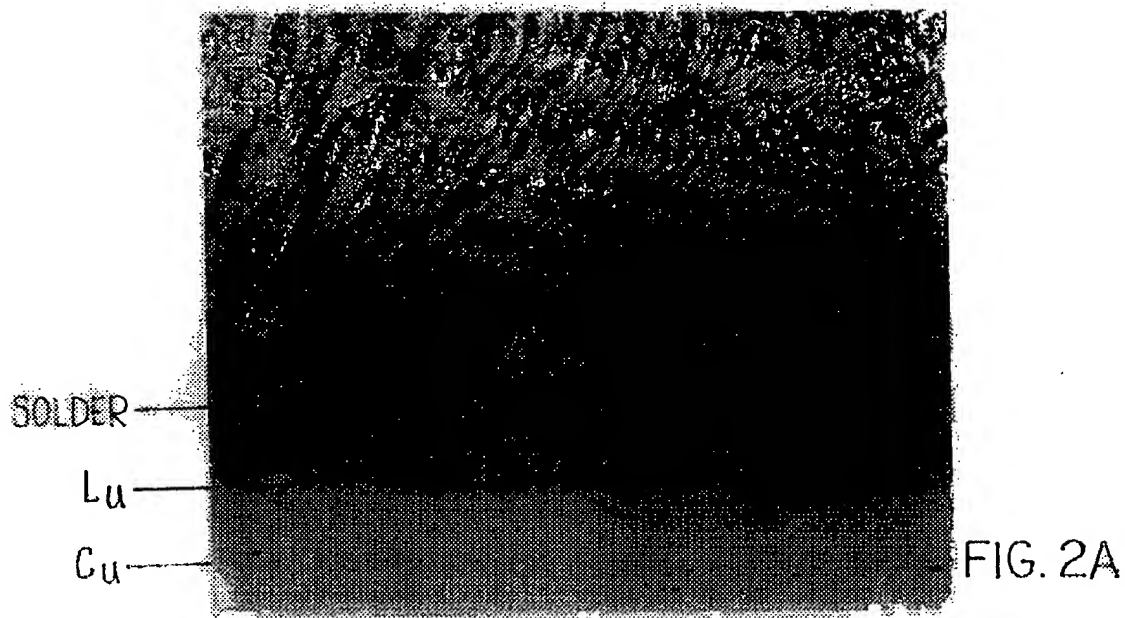


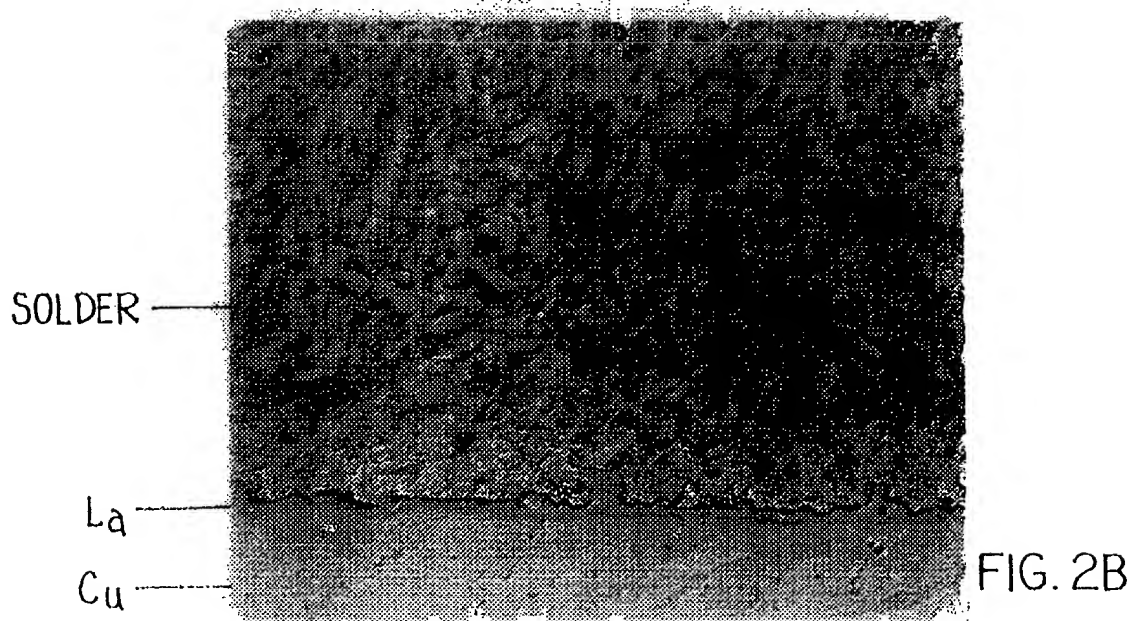
FIG. 1B

Aged Microstructure

2/5

 $99.85(\text{Sn}-4.7\text{Ag}-1.7\text{Cu}) + 0.15\text{Ni}$ DTA  $T_s \approx$  Similar to Sn-4.7Ag-1.7CuDTA  $T_l \approx$  Similar to Sn-4.7Ag-1.7CuWetting Angle Mean  $\approx 30.0^\circ$ Wetting Angle Range =  $28-34^\circ$ 

Unaged Microstructure



Aged Microstructure

3/5

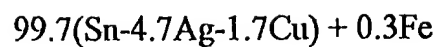
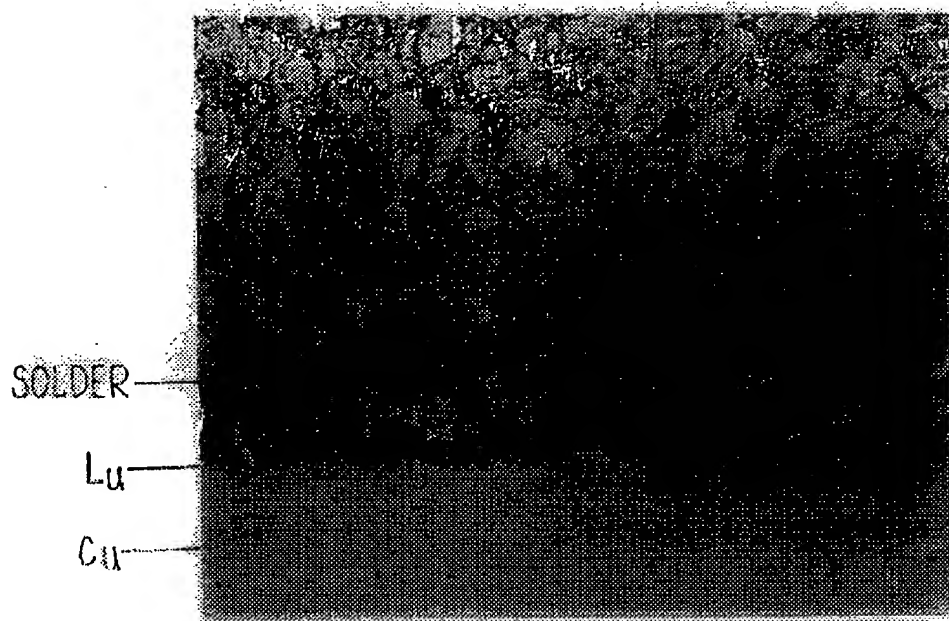
DTA  $T_g \approx$  Similar to Sn-4.7Ag-1.7CuWetting Angle Mean  $\approx 36.5^\circ$ DTA  $T_f \approx$  Similar to Sn-4.7Ag-1.7CuWetting Angle Range =  $27-45^\circ$ 

FIG. 3A

Unaged Microstructure

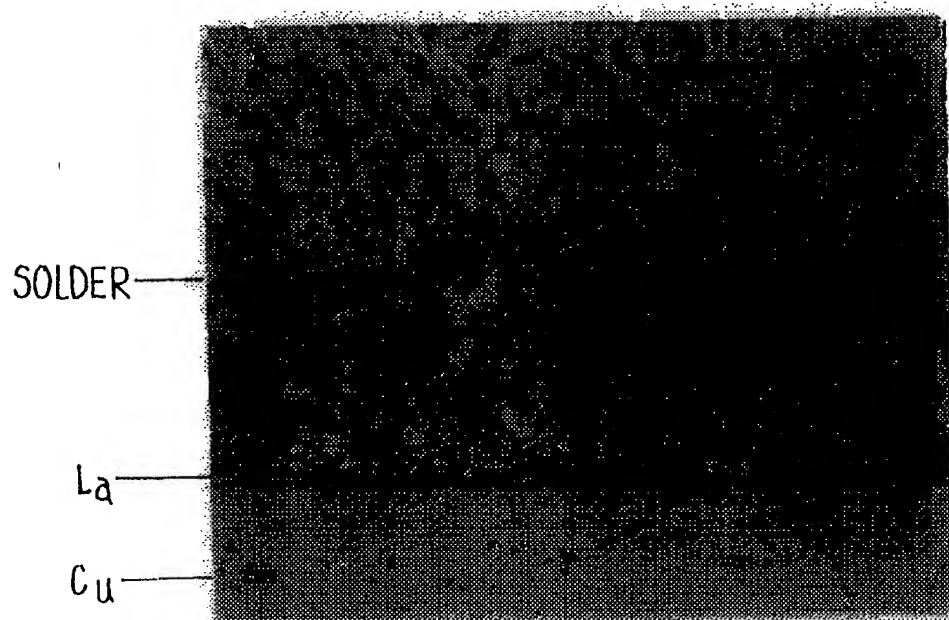
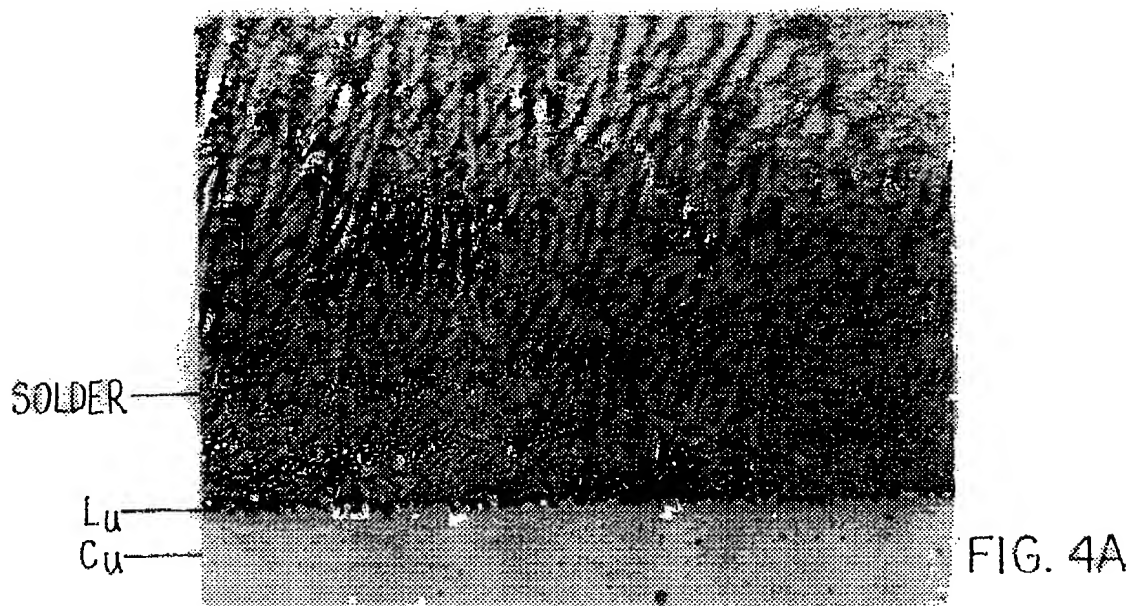


FIG. 3B

Aged Microstructure



4/5

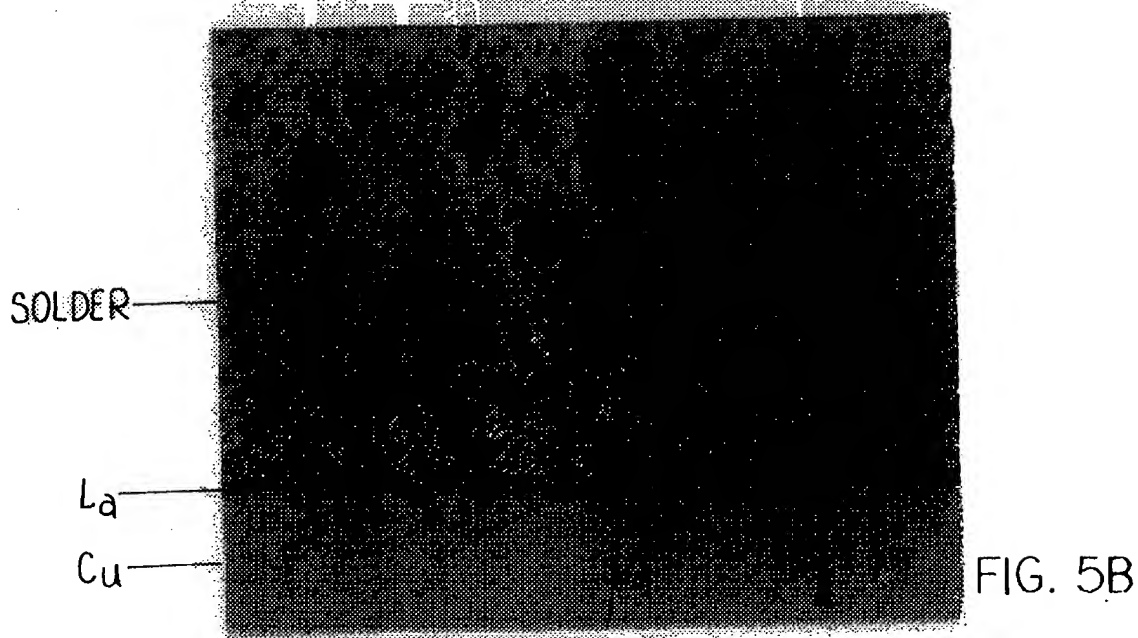
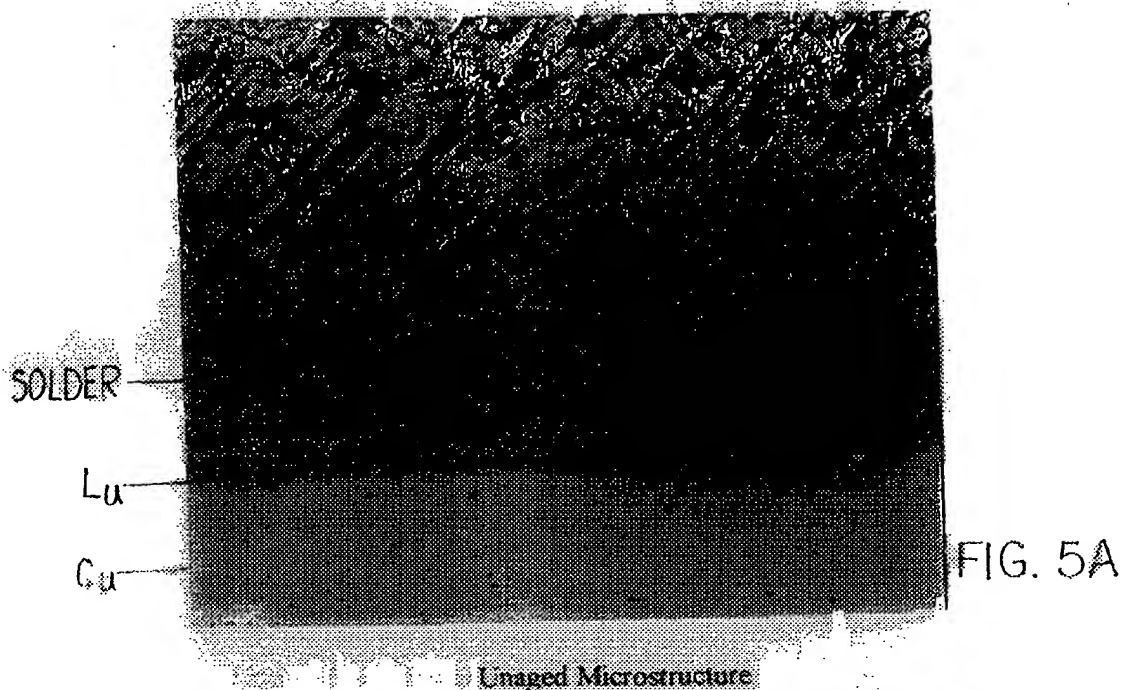
 $99.7(\text{Sn}-4.7\text{Ag}-1.7\text{Cu}) + 0.3\text{Ni}$ DTA  $T_s \approx 216.8^\circ\text{C}$ Wetting Angle Mean  $\approx 23.75^\circ$ DTA  $T_1 \approx 219.0^\circ\text{C}$ Wetting Angle Range =  $17-27^\circ$ 

Unaged Microstructure



Aged Microstructure

5/5

 $99.7(\text{Sn}-3.6\text{Ag}-1.0\text{Cu}) + 0.3\text{Ni}$ DTA  $T_s = 217.2^\circ\text{C}$ Wetting Angle Mean  $\approx 30.0^\circ$ DTA  $T_i = 219.2^\circ\text{C}$ Wetting Angle Range =  $29-32^\circ$ 

Aged Microstructure

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US98/02022

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B23K 35/26  
US CL : 420/557, 560, 561  
According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 420/557, 560, 561

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

REG, HCA, WPIDS, USPATFULL  
search terms: tin, Sn, copper, Cu, silver, Ag, iron, Fe, nickel, Ni

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,643,875 A (MIZUHARA) 17 February 1987, abstract.	1-19
X	US 4,758,407 A (BALLENTINE et al) 19 July 1988, abstract.	1-19
X	JP 08132279 A (MITSUI MINING & SMELTING CO LTD) 28 May 1996, abstract.	1-19
X	JP 06269983 A (HEISEI) 27 September 1994, abstract.	1-19

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*B* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

15 APRIL 1998

Date of mailing of the international search report

20 MAY 1998

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

SIKYIN IP

Telephone No. (703) 308-0654